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# PRACTICAL SIGNIFICANCE AND CALCULATION OF SURFACE TENSION OF GLASS, ENAMELS AND GLAZES

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15 P.

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16. Abstract

Surface tension is important in the formation of streaks and in the whole procedure of enameling and glazing, in the action of $TiO_2$ as opacifier, in the addn. of borax to enamels, or metals to glasses, and in the corrosion of refractories by molten charges. By use of known methods of measuring the surface tension the following additive consts. are found which give correct results within 1% with no discrepancy due to $B_2O_2$.

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## Practical significance and calculation of surface tension of glass, glazes and enamels*)

/82**)

There have been a number of important studies published on the measurement of the surface tension of fused silicates. The first measurements of glass were done a long time ago [G. Quincke[1)], 1868]; from 1910 onwards, and especially between 1935 and 1940, there have been several excellent studies on this subject. Recently, all these methods for measuring surface tension, together with their results, were discussed critically in context within the framework of a further experimental study done by G. Keppeler and A. Albrecht[2)].

In spite of all these previous basic scientific studies, up to now no-one has known what to do with all these measurements from a practical and theoretical point of view. There was, of course, no lack of qualitative indicators that when sharp edges are fused or when glass is blown and subjected to stress, surface tension is involved and is the reason that, for example, the pressed edges try to round themselves off or window glass tries to contract into a rod shape when it is being stretched into a wide panel[3)]. Other than this, there were in fact no other processes known in the fabrication of glass, glazes and enamels in which surface tension was significantly or even decisively involved. Thus, even Keppeler and Albrecht came to the conclusion: "Nevertheless, consideration of the significance of surface tension in relation to technology has not played any part in the selection of the composition of a glass". We also have a very incomplete picture of the effects and importance of

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*) By A. Dietzel (Report from the Kaiser Wilhelm Institute for Silicate Research, Berlin-Dahlem).

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For convenience, all footnotes are listed at the end of the article.

the surface tension of glass, glazes and enamels when they come into contact with solid or other liquid substances (interfacial tension). /82

In the following, therefore, I will first of all look at some examples that demonstrate how important, and even sometimes decisive, the effects of surface tension are.

Practical importance of surface tension

H. Jebsen-Marwedel[4] drew attention to the technical importance of surface tension in the process of glass fusion. At the beginning of the fusion process local fusion ("cells") of greatly varying composition takes place; a high interfacial surface tension inhibits homogenization. H. Jebsen-Marwedel[5] also correctly attributed another phenomenon of great technical importance to the determining effects of surface tension: the formation of streaks in glass. He was able to demonstrate graphically that "streaked glass" containing alumina, in which therefore rock substance is dissolved, in general has a higher surface tension than the mother glass, which means that an effort is made to form a ball (drop) or a strand (streak). If the situation were reversed, the "streaked glass" would then have a lower surface tension than the mother glass and almost no streaks would form, since then the foreign glass would try to surround the mother glass; i.e. distribute itself in it. Today we are able to add, on the basis of measurements of these observations of Jebsen-Marwedel, that the smaller effect of $SiO_2$ on surface tension compared with $Al_2O_3$ is responsible for the fact that streaks resulting from $SiO_2$ accumulation are not nearly as persistent in enameling as those that result from chamotte or other substances containing $Al_2O_3$. Therefore, in particularly sensitive areas it is advantageous to use quartz instead of chamotte.

Let us now turn to enamels. R.D. Cooke[6] has found that for base enameling it is absolutely essential to produce an oxide layer on the iron surface before the enamel softens, either

by burning treatment in an oxidizing atmosphere or by pre-oxidization of the iron, following which one carries out burning in a neutral atmosphere. A. Dietzel[7)] has been able to show that oxygen is primarily necessary for carrying out the electrolytic adhesion reactions. However, in this context the observation of A. Dietzel and K. Meures[8)] that is especially interesting is that the softening enamel wets only iron oxides but not the metallic iron. If one burns on an enamel in a vacuum or under reducing conditions, the enamel forms little balls and does not adhere.

The effects of surface tension became particularly obvious when a switch was made from majolica enamels containing lead to lead-free enamels. Of course, at that time the true reason for these problems was not known and people were working purely empirically with these lead-free substitutes, which involved a great deal of time and effort. Similar problems occurred when enamels containing boron were replaced by boron-free enamels. Today,we know that the success of lead-base enameling depends on controlling the surface tension of the enamel and that the attempts during the First World War to do enameling in the absence of boron were ultimately destined to fail completely because of inadequate understanding of these conditions. Today,it was at first thought that switching to boron-free enamels would cause problems in terms of fusibility, but it soon became apparent that as a rule it is possible to produce boron-free base and coating enamels that are entirely equal to enamels containing boron in their liquidity. At the same time,they are not so alkaline that their chemical resistance suffers; on the contrary, it is a surprising fact that has been confirmed in laboratory tests[9)] and from practical experience that in general,boron-free enamels are more chemically resistant than enamels that contain boron! However, a more important and extremely disturbing fault arose: boron-free enamels, especially base enamels, showed pores, craters, black spots and similar flaws. All these flaws can be attributed to the following phenomenon: During the enameling process,gas bubbles occur that burst during the burning process. An enamel

that contains boron immediately closes the opening (pore) that occurs; on the other hand, a normal boron-free enamel hardly flows into it or does not flow into it at all. The iron has a strong tendency to scale in these areas and forms the "black spots" mentioned above. The cause of this is the much greater surface tension of enamels that do not contain boron (310-340 /83
Dyn/cm) compared with enamels that contain boron (250-270 Dyn/cm[10]).
It is also worth noting that the borax substitutes that merely reduce the viscosity of the enamel soon disappeared from the market. What was needed was to lower the surface tension as well!

We will come back to these relationships later in this journal. It is enough to indicate here that these differences in surface tension also have a decisive and surprising effect on, for example, clouding with $TiO_2$ (and on gas clouding). It turned out that boron-free enamels possess higher solubility for $TiO_2$ than enamels containing boron. Nevertheless, clouding is much better in the boron-free enamels because the latter wet the $TiO_2$ particles poorly and therefore dissolve very slowly (see also a future issue of this journal).
In addition, the following phenomenon should be kept in mind: If a small amount of borax is added to a boron-free enamel in the milling, a favorable effect on pore formation is clearly discernible. However, this effect is not detectable when the same amount of borax is added by melting in the enamel frit. Borax used as a milling additive surrounds the glassy enamel particles with a borax membrane when the coating dries and this produces a lower surface tension "of the enamel" when the enamel melts.
The fusion-accelerating effect of borax that is used to advantage in the glass industry can be interpreted in the same way. The small amounts of 0.2-0.5% $B_2O_3$ that are used do in fact favorably affect the viscosity of the local fusion that takes place at the start of the melting process, up to a certain point; however, the wetting effect of the borax membrane undoubtedly has a decisive effect here also. It reduces the interfacial tension between the individual "cells" (Jebsen-Marwedel, see above)

and thus facilitates the melting process and homogenization. /83
This means that a requirement for a borax substitute that can improve the fusion process should also be that it not only reduce the viscosity of the initial local melting process or melt readily itself, but that it also lower surface tension.
The fusion of metal with glass is remotely related to the processes of enameling. The fact that glass containing lead or boron has proved to be particularly useful as fusion materials certainly depends partly, in the case of lead glass, on its "length" and its favorable electrical properties (low conductivity), loss angle). However, one should not overlook the fact that it was their very low surface tension and thus their very good wetting capacity compared with the (superficially oxidized) metals that are to be fused that was the determining factor in the choice of these types of glass. The fundamental importance of the wetting of the oxidized metal by the glass in relation to the fusion problem has been demonstrated, for example, by B.W. Espe*) in his detailed analyses.
Another problem that involves the decisive effects of surface tension is the saturation and subsequent corrosion of fire-resistant building materials by melting (mixed dust, glass, slags, etc.). In this case also, up to now attention has only been paid to the - undoubtedly significant - effects of viscosity. However, it occurs to one that, besides the fluidity, the "capillary constant"; i.e. the surface tension, must also be important for the "absorption" of the fused material into the porous stone. In addition, one should look at the studies of Jebsen-Marwedel[11)] that show that surface tension is an important factor from another point of view in the corrosion of fire-fesistant stone by glass fusion. Since the streaked coating on the stone has a high surface tension, it attempts while it is flowing downwards to contract at the same time in such a way that this protective film on the upper side of the stone becomes very thin, while the streaked glass collects along the vertical surface of the stone. This explains the greater effect of the glass fusion on the upper part of the stone.

Finally, one has to remember that in many respects the effects of surface tension are the same for ceramic glazes as they are for enamels. The "sheen"; i.e. the smoothness or evenness of a glaze, is determined, as with enamels, not only by the degree of light refraction but also by surface tension. Another example of the effects of surface tension is the so-called "peeling" of glazes. /83

## Ways of measuring surface tension

In view of this fairly fundamental importance of surface tension, the question arises as to what methods are available, especially in practice, for measuring the surface tension of a glass, enamel or glaze, or, in reverse, what one has to do in order to obtain an enamel with a certain surface tension.
One method is by measurement. However, the measuring methods are laborious and time-consuming and have to await further systematic research. Another method - and a surprisingly successful one - is the calculation of the surface tension from the chemical composition,using factors. This conceivably simple method will be of particular interest to the smelter.

## Calculation of the surface tension

E.W. Tillotson[12)] has already assumed that the surface tension of a glass is composed additively of the values for the individual oxides according to their percentages. He calculated this value using factors, in the same way as, for example, is already generally known for expansion. According to Tillotson, the following factors should be used: for each 1% of CaO, 3.2 Dyn/cm; for BaO 2.0; for $Na_2O$ 1.6; for $SiO_2$ 1.3;and for $B_2O_3$ 0.45. Keppeler and Albrecht[2)] have recently shown that a factor of 2 is missing from Tillotson's formula, so that the above values should be doubled. At the same time, these authors were doubtful about the correctness of the assumption made by Tillotson, namely the additive constitution of the surface tension, although the value for 100% $B_2O_3$ (= 85 Dyn/cm) would also be produced surprisingly well by means of calculation. It is amazing that

Table I. /83

Additive calculation of surface tension in Dyn/cm for 900°.

| [1] Faktoren für je 1 Gew.-%: | | | | | |
|---|---|---|---|---|---|
| $Li_2O$ | 4,6 | $B_2O_3$ | 0,8 | $Fe_2O_3$, CoO, NiO, MnO | 4,5 |
| $Na_2O$ | 1,5 | $Al_2O_3$ | 6,2 | | |
| $K_2O$ | 0,1 | $SiO_2$ | 3,40 | | |
| MgO | 6,6 | $TiO_2$ | 2,9 | | |
| CaO | 4,8 | $V_2O_5$ | —6,1 | | |
| BaO | 3,7 | $ZrO_2$ | 4,1 | | |
| PbO | 1,2 | $CaF_2$ | 3,7 | | |
| ZnO | 4,7 | | | | |

[2] Für je + 100° sind 4 Einheiten am Gesamtergebnis abzuziehen.

Key: 1 factors for each 1% by weight;

2 For each +100°,4 units should be subtracted from the total result.

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this method, which was discovered more than 30 years ago, has not been pursued any further until now.

The factors given in Tab. I for calculating the surface tension at 900° were obtained from the currently available reliable measurements of A.E. Badger, C.W. Parmelee and A.C. Williams[13], C.W. Parmelee, K.C. Lyon and C.G. Harman[14], G. Keppeler[15] and Albrecht[2]. (The method of calculation is the same one used for expansion.) In order to be able to convert for another temperature, a temperature correction has to be made: for each temperature increase of 100°, 4 units should be subtracted from the result.

The following example of calculation will serve to explain the method: The surface tension for a glass of 74% $SiO_2$, 10% CaO and 16% $Na_2O$ at 1400° can be calculated as follows:

| | | |
|---|---|---|
| $SiO_2$ | $74 \times 3{,}40 =$ | 252 Dyn/cm |
| CaO | $10 \times 4{,}8 =$ | 48 „ |
| $Na_2O$ | $16 \times 1{,}5 =$ | 24 „ |
| | | 324 Dyn/cm für 900°. |

[fuer = for]

Table II

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Comparison of calculated and measured values for surface tension at various temperatures.

A = analysis values; S = synthesis values; T = partially analyzed (a few oxides) [Key on foll. page]

| Nr. | | $SiO_2$ | $B_2O_3$ | $Al_2O_3$ | MgO | CaO | | | | $Na_2O$ | $K_2O$ | Temperat. t° | 1 Oberflächenspannung gemessen 2 | 3 berechnet 900° | 3 berechnet t° | 4 Differenz gemessen 2 − berechnet 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 Messungen von Badger, Parmelee und Williams | | | | | | | | | | | | | | |
| 1. | A | 74,8 | — | 0,4 | 3,2 | 4,8 | BaO | — | PbO | 16,8 | — | 1350° | 302 | 324 | 306 | − 4 |
| 2. | A | 68,0 | — | 0,3 | — | 0,3 | 1,4 | — | 17,7 | 5,8 | 8,5 | 1350° | 245 | 263 | 245 | 0 |
| 3. | A | 72,5 | — | — | — | 10,1 | $CaS_2$ | | $(Mn,Ca,Ni)O$ | 17,4 | — | 1350° | 302 | 320 | 302 | 0 |
| 4. | S | 41,0 | 17,9 | 7,9 | — | 3,4 | 7,2 | | 2,3 | 15,7 | 4,6 | 925° | 246 | 279 | 278 | − 32 |
| | | 6 Messungen von Parmelee und Harman | | | | | | | | | | | | | | |
| 5. | A | 73,2 | — | — | 3,0 | 7,8 | — | — | — | 16,0 | — | 1400° | 305 | 327 | 307 | − 4 |
| 6. | A | 71,7 | — | 2,0 | 3,0 | 7,6 | — | — | — | 15,7 | — | 1400° | 317 | 333 | 313 | + 4 |
| 7. | A | 70,4 | — | 3,8 | 2,9 | 7,5 | — | — | — | 15,4 | — | 1350° | 325 | 340 | 322 | + 1 |
| 8. | A | 67,8 | — | 7,4 | 2,8 | 7,2 | — | — | — | 14,8 | — | 1400° | 352 | 350 | 350 | + 2 |
| | | 1 Messung von Parmelee und Lyon | | | | | | | | | | | | | | |
| 9. | A | 64,9 | 13,0 | 1,5 | — | — | — | — | — | 18,6 | — | 1250° | 258 | 267 | 253 | − 5 |
| | | 8 Messungen von G. Keppeler | | | | | | | | | | | | | | |
| 10. | T | 75,9 | — | 1,4 | — | 8,9 | — | — | — | 13,8 | — | 1400° | 321 | 330 | 310 | + 11 |
| 11. | T | 74,4 | 1,5 | 1,4 | — | 8,9 | — | — | — | 13,8 | — | 1400° | 311 | 325 | 305 | + 6 |
| 12. | T | 72,8 | 3,0 | 1,4 | — | 8,9 | — | — | — | 13,8 | — | 1400° | 302 | 322 | 302 | 0 |
| 13. | T | 72,3 | 3,8 | 1,4 | — | 8,8 | — | — | — | 13,7 | — | 1400° | 301 | 320 | 300 | + 1 |
| 14. | T | 68,5 | 7,2 | 1,4 | — | 9,0 | — | — | — | 13,9 | — | 1400° | 289 | 311 | 291 | − 2 |
| 15 | T | 68,2 | 9,1 | 1,5 | — | 9,1 | — | — | — | 14,0 | — | 1400° | 278 | 306 | 286 | − 8 |
| | | 9 Messungen von Parmelee, Lyon und Harman | | | | | | | | | | | | | | |
| 16. | A | 59,9 | 7,0 | 4,7(0) | — | — | — | — | — | 27,1 | — | 1200° | 248 | 279 | 267 | − 19 |
| 17. | A | 71,8 | 3,8 | 3,9(0) | — | — | — | — | — | 20,4 | — | 1200° | 277 | 310 | 298 | − 21 |
| 18. | A | 54,9 | 18,7 | 2,0 | — | — | — | — | — | 21,9 | — | 1200° | 255 | 247 | 255 | 0 |
| 19. | A | 64,9 | 13,0 | 1,6 | — | — | — | — | — | 18,6 | — | 1200° | 253 | 268 | 256 | − 3 |
| 20. | A | 74,1 | 11,0 | 1,3 | — | — | — | — | — | 13,4 | — | 1200° | 268 | 289 | 277 | − 9 |
| 21. | A | 59,0 | 22,7 | 2,1 | — | — | — | — | — | 14,6 | — | 1200° | 235 | 253 | 241 | − 6 |
| 22. | A | 69,2 | 17,5 | 1,9 | — | — | — | — | — | 10,2 | — | 1200° | 256 | 275 | 263 | − 7 |
| 23. | S | 60,0 | — | — | — | — | — | — | — | 40,0 | — | 1300° | 291 | 264 | 248 | + 43 |
| 24. | S | 49,2 | — | — | — | — | — | — | — | 50,8 | — | 1300° | 307 | 243 | 227 | + 80 |
| 25. | S | 66,0 | — | — | — | — | — | — | — | 34,0 | — | 1300° | 282 | 275 | 259 | + 23 |
| 26. | S | 73,6 | — | — | — | — | — | — | — | 26,4 | — | 1300° | 277 | 290 | 274 | + 3 |
| 27. | S | 80,0 | — | — | — | — | — | — | — | 20,0 | — | 1300° | 281 | 302 | 286 | − 5 |
| 28. | S | 76,0 | — | — | — | 5,0 | — | — | — | 19,0 | — | 1300° | 296 | 310 | 294 | + 2 |
| 29. | S | 72,0 | — | — | — | 10,0 | — | — | — | 18,0 | — | 1300° | 306 | 320 | 304 | + 2 |
| 30. | S | 62,2 | — | — | — | — | — | — | — | 37,8 | — | 1300° | 284 | 269 | 253 | + 31 |
| 31. | S | 63,8 | — | — | — | 6,2 | — | — | — | 30,0 | — | 1300° | 301 | 292 | 276 | + 25 |
| 32. | S | 56,6 | — | — | — | 5,6 | — | — | — | 37,8 | — | 1300° | 298 | 277 | 261 | + 37 |
| 33. | S | 59,1 | — | — | — | 13,1 | — | — | — | 27,8 | — | 1300° | 313 | 307 | 289 | + 24 |
| 34. | S | 53,0 | — | — | — | 11,7 | — | — | — | 35,3 | — | 1300° | 313 | 289 | 273 | + 40 |
| 35. | S | 50,5 | — | — | — | 15,8 | — | — | — | 33,7 | — | 1300° | 322 | 299 | 283 | + 39 |
| 36. | S | 56,1 | — | — | — | 17,5 | — | — | — | 26,4 | — | 1300° | 322 | 315 | 299 | + 23 |
| 37. | S | 64,0 | — | — | — | 20,0 | — | — | — | 16,0 | — | 1300° | 325 | 338 | 322 | + 1 |

Key to Tab. II: /84

1 surface tension; 2 measured; 3 calculated; 4 difference;
5 Measurements of Badger, Parmelee and Williams;
6 Measurements of Parmelee and Harman;
7 Measurements of Parmelee and Lyon;
8 Measurements of G. Keppeler;
9 Measurements of Parmelee, Lyon and Harman.

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For a temperature increase from 900° to 1400°, 5x4 = 20 units should be subtracted from the total, so that the surface tension for the glass described at 1400° is 304 Dyn/cm. The following examples (Tab. II) serve to show the agreement between calculation and measurement. I have listed in particular glasses that are of widely differing compositions.

As one can see, the calculated surface tensions agree in every case with the measured values to within ±3 units on average where the the glass composition was sufficiently exactly known; i.e. where it was possible to make the calculations using analysis values. Glass types 16 and 17 have also been analyzed, but one is justified in nursing some doubt here, since the analyses of the syntheses differ substantially in the $Al_2O_3$ content; and it is alumina that has an enormous effect on surface tension. On the other hand, however, the values for many other types of glass agree well that were not analyzed or were only partially analyzed (nos. 11-14, 26-29, 37) and in which one does not need to assume any significant deviations in composition. However, the importance of knowledge of the composition is demonstrated by the study of Parmelee, Lyon and Harman (nos. 23-37). Using their measured values, these authors prepared graphs with hosts of curves and from these drew inferences as to the effects of the individual oxides. According to this, it appeared that one could not assume any additivity for the surface tension. However, these conclusions are based on syntheses and should therefore be accepted with caution, at least in the case of glass types with soda levels of 20-50°, because of the high degree of alkali evaporation that can be expected. In addition, it is on the surface

that the amount of alkali is reduced, and where the measurements are carried out! The devitrification measurements and analyses of A.Dietzel[16] have shown that the loss of alkali is already detectable in microscopically measurable surface layers when there is 14-18% $Na_2O$ in the glass; of course, on average the loss was only 0.8-2.0% $Na_2O$. However, one can see that glass types with high soda contents,such as were used by these authors, in some cases will demonstrate a much higher degree of evaporation and that in these cases one cannot classify the measured surface tension as the synthesis value at all for the interior of the glass, and strictly speaking not even as the analysis value. This makes it very clear that differences between the /85
measured and calculated values for the surface tension increase with increasing alkali content. Figure 1 shows the differences according to Tab. II in relation to the alkali levels. One can see only an increase in the alkali content over about 20% makes itself noticeable. There is obviously a parallel here with the observations made in devitrification experiments[16]; it is also above a certain alkali level that evaporation suddenly apparently has an effect.

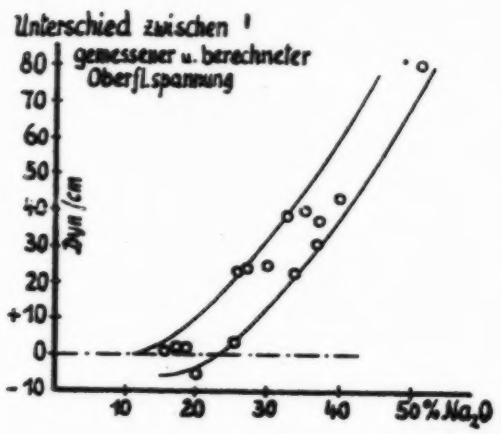


Fig. 1.

Key: 1 Difference between measured and calculated surface tension.

Once the validity of additive calculation of the surface tension has thus been adequately demonstrated, it is permissible to calculate, in reverse, from the measured surface tension of, say glass no. 23, with a nominal level of about 40% $Na_2O$, the actual alkali content. One obtains a value of only 20% $Na_2O$ for the surface layer. Similar calculations can also naturally be done for the other melting proce ~es. /85

## Conclusions

All in all, one can therefore establish that the surface tension can in fact be calculated additively from the percentages of the individual oxides, and with a surprising degree of accuracy that is not much lower than that of the measurement method.
It goes without saying that one is inclined to entertain the same fundamental doubts that have been justifiably voiced relative to additive calculation of, for example, expansion[17], density, light refraction, etc. Meanwhile, one should take note of the highly interesting fact from a structural-theoretical point of view that, according to the measurements available (and on account of the admissibility of the additive calculation method), surface tension is so far probably the only property of glass that does not demonstrate any boric acid anomaly![18]. This circumstance already tells us that here on the surface the conditions are somewhat different from those to which we are normally accustomed.
Aside from these theoretical questions, the primary significance of this report may lie in the fact that the smelter thereby obtains a conceivably simple method for controlling by calculation the otherwise hard to measure and yet so important, from a practical point of view, surface tension; or of preparing batches that supply with sufficient accuracy glazes or enamels with the desired surface tensions.
Thus, using the factors alone one can already see that in all cases where a low surface tension is desirable (base enamels) MgO in particular, and possibly also ZnO and CaO, can be appropriately replaced by BaO; while $Al_2O_3$ can be replaced by $SiO_2$ or $TiO_2$; and $Na_2O$ can be partly replaced by $K_2O$, etc.

It is then easy to reduce the surface tension from 320 or 330 Dyn/cm to levels below 290 or 280 Dyn/cm, as is necessary for boron-free enamels[19]. /85

It is expected that this calculation method will make a significant contribution to solving the problems that are still involved in boron-free enameling.

Summary

1. The great practical significance of surface tension in glass and enamel technology and in ceramics is demonstrated using various examples; sometimes it is considerably involved in processes where up to now attention has only been paid to the viscosity. From this point of view, there is a brief discussion of the effects of the agents used to facilitate fusion; of streak formation, processes used in boron-free enameling and the fusion of glazes or in the addition of borax to the enamel slip; and the problem of corrosion of fire-resistant stone resulting from the effects of fused coatings.
2. Using known surface tension measurements, factors are given for additive calculation of the surface tension from the composition, including temperature correction. The accuracy is surprisingly good and is within 3 units on average (= 1% of the value).
3. Attention is drawn to the fact that surface tension is the only property that does not demonstrate any boric acid anomaly.
4. This calculation method provides for practical use a simple means of analyzing questions of boron-free enameling, improving fusion, etc., using relative exact numerical data for the surface tension.

Footnotes and references

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8) Sprechsaal 66 (1933), 647, esp. p. 651 and note 15.
9) A. Dietzel, R. Boncke, W. Pralow, Sprechsaal 74 (1941), 453.
10) For the sake of comparison, the following figures are given: surface tension of mercury = 500, molten boric acid = 85, organic liquids - around 20-40 Dyn/cm. /83
*) Feinmechanik und Praezision 47 (1939), p. 225. Some of the views presented here on the adhesion of enamels have been superceded, however; see A. Dietzel, Sprechsaal 68 (1935), p. 3.
11) Glastechn. Ber. 15 (1937), p. 163, esp. p. 170.
12) J. Ind. Eng. Chem. 3 (1911), 631; 4 (1912), 651.
13) J. Amer. Cer. Soc. 20 (1937), 325.
14) Univ. Illinois Bull. 36 (1939), no. 81.
15) J. Soc. Glass Techn. 21 (1937), 53.
16) Glastechn. Ber. 19 (1941), 257. /84
17) For structural-theoretical basis, see A. Dietzel, Glastechn. Ber. 19 (1941), 319. /85
18) This phenomenon is the result of the energetic instability of the $[BO_4]$ coordination on the surface. I will return to a more detailed explanation of this at another time.
19) It should be mentioned that the surface tension can also be lowered - although it cannot be controlled - by means of gases ($SO_2$) or by additives that produce these gases (sulfides, sulfur, sulfites, etc.).